63-2-3

TECHNICAL INFORMATION SERIES

R62SD57

THE PYROLYSIS OF PLASTICS IN A HIGH VACUUM ARC IMAGE FURNACE II

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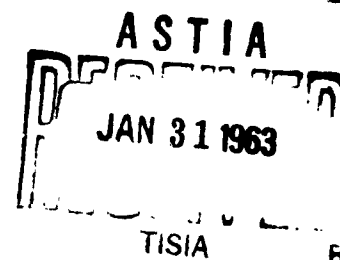
SPACE SCIENCES LABORATORY

GENERAL ⊛ ELECTRIC

MISSILE AND SPACE DIVISION

SPACE SCIENCES LABORATORY

AEROPHYSICS SECTION

THE PYROLYSIS OF PLASTICS IN A HIGH VACUUM
ARC IMAGE FURNACE. II.[*]

by

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R62SD57 - Class I
December 1962

MISSILE AND SPACE DIVISION

GENERAL ELECTRIC

CONTENTS

ABSTRACT

Samples of glass and nylon reinforced CTL 91-LD Phenolic and G. E. 124 Resin were pyrolyzed in an arc image furnace at high vacuum. Compositions of the various degradation gases are reported. Average molecular weights of these gases were calculated. A description of the mechanism of pyrolysis of G. E. 124 Resins is presented. A critique of the method is included.

I. INTRODUCTION

The purpose of this study is to obtain chemical compositions of pyrolysis gases that would be injected into the boundary layer that surrounds ablating plastics. The results of studies of arc image furnace degradation of non-reinforced and glass reinforced CTL 91-LD* Phenolic in high vacuum were published in Reference 1. These studies are extended to the nylon reinforced phenolic and formulation #124 of the General Electric Company Century Series Resins in this paper. The results of further pyrolyses of the glass reinforced phenolic are also reported.

* A product of Cincinnati Testing and Research Laboratory.

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II. EXPERIMENTAL

The apparatus and analytical techniques that were employed were essentially the same as those that were used in References 1 and 2. The arc image furnace consisted of a pair of General Electric Company 60-inch diameter search light mirrors. The carbon arc source was able to supply a maximum flux of about 400 BTU/ft^2 sec. to the 1/2 inch diameter surface. Some modifications were made in the vacuum system, as may be seen by comparison of Figure 1 with Figure 2 of Reference 1. In the earlier work, the non-condensable gases were removed from the vicinity of the hot plastic by expansion into a surge volume. These gases were then completely transferred to a sample flask by Toepler Pump, and were allowed to stand so that the gases became thoroughly mixed. A P-V-T measurement served to determine the total yield of non-condensables. In the present work, the non-condensables were pumped into a pre-evacuated expansion volume, as they formed, with a Consolidated Electrodynamics Corporation Model GHG 15-S Diffusion Pump. This pump was able to function against a maximum fore pressure of between 5 and 10 mm Hg. When transfer was completed, the pump was used to circulate the gases in order to mix them. P-V-T measurements were used to determine yields, but in this case, the pressure was measured in the expansion volume with a McLeod Gauge. The new procedure was far less cumbersome than the earlier method.

In the earlier work, zero time was defined as the time when the arc became stable. A crude shutter was used to determine zero time in

the present work. The quartz dome was covered with a pair of cardboard sheets, that were themselves covered with aluminum foil, before the arc was struck. The sheets were fastened to each other with masking tape. A long string was attached to each sheet. When the discharge was stable, the cardboard sheets were quickly pulled away from the quartz dome and quickly dropped to the floor of the furnace housing. Zero time was defined as that when the shutter was withdrawn. Exposure time was the interval between zero time and the instant when the arc was extinguished.

The volatile degradation products were once again divided into three fractions. The first fraction was volatile at liquid nitrogen temperature. The second fraction was volatile at CO_2 ice-trichloroethylene bath temperature ($-78^{\circ}C$) after the first fraction was removed. The third fraction consisted of the balance of the products that were volatile at room temperature. Quantitative analysis of the first fraction was performed by chromatography. Qualitative analyses of second and third fractions were performed by infrared absorption spectroscopy and a combination of chromatography with time-of-flight mass spectroscopy. Quantitative analyses of second and third fractions were performed by mass spectroscopy. Ammonia in second fractions of the phenolics was analyzed by absorption in anhydrous oxalic acid. Total yields of third fractions were determined gravimetrically in small tubes.

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III. MATERIALS

Both reinforced phenolics contained about 40% phenolic by weight. 6,6 nylon was used. The 1/2 diameter by 1 inch long cylinder samples were machined so that the cloth reinforcement was perpendicular to the circular faces. The G. E. 124 Resin samples were machined from cast rods.

IV. RESULTS

The results of these experiments are listed in Tables 1-4. Table 1 contains a general summary of all runs carried out for the three materials, including quantitative analyses for first fractions, and ammonia for the phenolics. Tables 2-4 show quantitative compositions for all experiments where second or third fractions were analyzed. Products are listed in order of increasing molecular weight.

V. DISCUSSION

Examination of Table 1 shows that experiments which were carried out for the same exposure time on samples from the same batch had a reasonable degree of reproducibility with respect to total weight loss, total yields of the various fractions, and the specific analyses of non-condensable components and ammonia. The ten second exposure runs for glass phenolic were not very different from the ten second run of Reference 1 (Table 1 - Run 4). The specific analyses of the condensables, as listed in Tables 2-4, were quite reproducible for most components, but there were some marked differences. Some of these differences may have been due to different interpretations of the mass spectra from the two different analytical laboratories. In the case of G. E. 124 Resin (Table 4), the sample from Run 56 is from a different batch than the other samples. It is thought, also, that some of the differences may be due to chemical reactions which occurred between the various products while standing. It is interesting to note that, in some cases, fractions of product formed brown solids while standing, while other fractions, which one might assume to be identical, did not*. The most evident differences are H_2O for the glass phenolic in Runs 51 and 52 and acrolein for the nylon phenolic in Run 49. Mass spectroscopy

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* Recent flash pyrolysis studies of glass reinforced phenolic in the reaction chamber of a time-of-flight mass spectrometer have shown that sulfur dioxide is a decomposition product. 0.1 per cent sulfur was found by subsequent chemical analysis. It seems likely that sulfur dioxide reacted with ammonia in the presence of water in the traps to form ammonium sulfite. It is also possible that ammonia reacted with some of the carbon dioxide to form ammonium carbonate. Therefore, at least in the case of the glass reinforced phenolic, the reported quantity of ammonia is too low, carbon dioxide may be too low, and sulfur dioxide is completely missing.

would be expected to be comparatively inaccurate when applied to fractions which contain a large percentage of water. Tables 2-4 also list material balances for all cases where the first and second fractions were analyzed in detail. For glass reinforced phenolic (Table 2) Runs 38 and 51, 86.8 and 87.6 per cent of the weight loss was accounted for by the three volatile fractions. It is reasonable that these should be less than 100 per cent since some glass was also lost, and since some products which were not volatile at room temperature were observed on the surface of the quartz dome and on the pyrex wool filter of the first trap. For nylon reinforced phenolic (Table 3) Runs 39, 49, and 50, 98.5, 99.8 and 102.7 of the weight loss appeared in the volatile fractions. These represent extremely good agreement. For G. E. 124 Resin (Table 4) Runs 41, 42, and 56, 88.4, 82.3, and 101.3 per cent of the total weight loss was accounted for. Sample 56 was not only from a different batch than samples 41 and 42, but mass spectroscopy of the second fractions was carried out in different laboratories. Since a small amount of products are observed on the quartz dome and in the pyrex wool of the first trap in all cases, it may be that the material balances for nylon-phenolic and Run 56 are slightly high. However, it is more probable that those for Runs 41 and 42 of the G. E. 124 Resin are a little too low. Table 5 contains the average of all analytical data and average molecular weights for products which were volatile at room temperature for each plastic for ten second runs. The real molecular weights for stable products would be a little higher because the non-volatile products have comparatively high molecular weights. Run 56 has been included for G. E. 124

Resin even though it was from a different batch than the other samples, because the data were not very different. The differences between decomposition products of glass and nylon reinforced phenolic are interesting. Although most components are produced in quite similar amounts, more CO_2, HCN and unsaturated hydrocarbons are produced in the case of nylon. These products are reasonable degradation products of nylon. Gruntfest[3] observed similar differences for arc image furnace pyrolyses of nylon and Refrasil reinforced CTL 91-LD phenolics.

Barry and Gaulin[4] studied the ablation of Century Series Resins as a function of pressure and heat flux in several arc plasma facilities and rocket exhaust. Under low pressure and low heat flux conditions, chars were found to contain rather large pores with thick walls with a broad distribution in pore diameter. At high pressures and heat fluxes, chars were more porous with a homogeneous distribution of smaller pores. Pyrolysis studies showed that the chars formed by a two step process. The first was the production of a highly cross-linked foam at about $350^{\circ}C$, with the evolution of high molecular weight products. This was followed by a further decomposition at higher temperatures to form a more highly carbonaceous char, which was accompanied by the evolution of hydrogen and carbon monoxide. These authors likened the foaming process to the production of polyurethane foams. For slow rates of foaming, small pores have time to break and form larger pores with thick walls. Foaming under vacuum also tends to produce large pores since the escape of gas is

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accelerated with the material in a very fluid state. Speeding up the process, with increased pressure, tends to give foams of uniformly fine pore structure, with low density and thin walls, if sufficient foaming volatiles are available.

Arc image furnace pyrolyses are carried out under low pressure and high heat flux conditions. Microscope photographs of three char zones are shown in Figure 2. The region closest to the front surface appears to have a combination of the two types of chars that were described by Barry and Gaulin. While there were a few large pores, a bulk of the char appeared to have rather fine uniform pores. The interior char, however, had the characteristic appearance of the low heat flux, low pressure types. Although the front surface of the char had some small fissures, there were many very large fissures which opened to the sides of the sample between the front surface and the virgin plastic. The chars which were produced in the arc image furnace appeared to be superficially similar to those that were produced by Barry and Sutton[5] by passing the hot plasma from an air-stabilized arc through the interior of cylindrical test specimens which had been bored.

Barry and Gaulin[4] pyrolyzed samples of pulverized G. E. 123 Resin, a somewhat different formulation from the 124 Resin, in an evacuated tube to temperatures slightly below 1000°C. Product analysis was performed for some of the fractions. H_2 was not observed as a reaction product until temperatures of about 600°C were reached. Although experiments at

lower temperatures were of longer duration, it took a variety of times from 167 to 280 seconds to heat samples from room temperature to the final elevated temperatures. Comparison of the relative yields of H_2 with CO, CH_4, and CO_2 showed that their product picture was most like those of the arc image furnace experiments at about $700^{\circ}C$. These authors showed that the maximum char temperatures of various parts of low heat flux low pressure chars did not exceed 300 to $600^{\circ}C$, and predicted that the gases that would be injected into the plasma stream would have compositions similar with tube furnace experiments that were carried out at these temperatures. High heat flux, high pressure chars were shown to exceed $1000^{\circ}C$. Low temperature decomposition products of G. E. 123 Resin were also allowed to percolate through a char which was generated from 126 Resin while the char was heated to above $2250^{\circ}C$ with an induction heater. Eighty-five per cent of the available hydrogen was recovered as H_2, while eighty-six per cent of the available oxygen was recovered as CO. Very small amounts of CH_4, C_2H_4, and C_2H_2 were formed.

Examination of Table 1 shows that the rate of loss of weight of 124 Resin was higher for the 10 second exposure than for 5 seconds. Although the rates of formation of CH_4, the second, and third fractions also increased with increased exposure, those for H_2 and CO decreased. Analysis of the various factors leads to the following description of the pyrolysis of G. E. 124 Resin in the arc image furnace.

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The application of the high heat flux at the front surface of the sample led, initially, to the rapid formation of a highly cross-linked porous char with a comparatively homogeneous distribution of small pores. The presence of vacuum caused larger pores to form in a small fraction of this zone, and some small fissures resulted. As pyrolysis continued, the effective heat flux which reached the lower regions was reduced. Because the formation of the porous char was slower, the vacuum environment caused the more fluid char pore to break and form larger pores with thick walls. The gases were released from these lower temperature regions through large fissures in the cylindrical wall of the sample. For the shorter exposures, the relative quantity of the higher temperature degradation, which led to the formation of H_2 and CO, was more important than for the longer exposures, where the lower temperature degradation processes assumed greater importance. Although the front surface of the sample was probably heated to above $2000^{\circ}C$, the final product picture for the 10 second run was more representative of heating at $700^{\circ}C$. It is likely that very short exposures would yield products that are more representative of higher temperature degradation.

Although it was not tested in any systematic fashion, the installation of the C.E.C. Model GHG 15-S diffusion pump did not appear to influence the results of the experiments. It is possible that this pump did not influence the pumping rate appreciably since the 1-1/2 meter length of 1/2 inch diameter tubing was allowed to remain between the dome and the first trap. Changing of this tubing would have meant a major modification of the vacuum system. Enlargement at the dome could have caused interference

with focussing. Perhaps a cylindrical configuration could have been used

instead of spherical. The use of much larger tubing, or pipe, would have

made handling the system more difficult. Another possibility could be

to remove the gases through the back. Placement of the vacuum system with

respect to the source and furnace housings could then be a problem. It

is possible, however, that even very efficient pumping would not change

the situation. The pressure at the face of the sample during pyrolysis

may be so high compared to the pressure of the surrounding region that

very few molecules would find their way back to a region which is hot

enough to cause an appreciable change in the initial stable products.

VI. CONCLUSIONS

These studies and the work of Reference 1 have shown that it is possible to obtain reasonably reproducible product compositions of high temperature pyrolysis products of plastics with an arc image furnace and with a variety of analytical techniques. Several factors limit the degree of reproducibility that may be achieved. It is very difficult to reproduce focussing of the arc because of the inherent instability of arcs and the cumbersome 60 inch mirror housings. Shuttering is a real problem with the large mirrors. One would suspect that the table top type of arc image furnace would be superior for such studies. As decomposition progresses, the position of the front surface of the plastic sample will change. This will change the energy input. Illumination of the sample face is not absolutely uniform. Uniformity and quantity of illumination are influenced by the decomposition products that are deposited on the surface of the dome. Since decomposition products arise from regions which are at different temperatures and states of decomposition simultaneously, interpretation of the data is difficult. This difficulty is enhanced by the large number of products. It might be helpful to instrument the samples to determine temperature at a variety of distances from the surface; however, interpretation of data will be difficult because of the other factors.

In order to evaluate the ability of a given plastic to withstand ablation, one must know the precise chemical composition of the gases that are injected into each part of the boundary layer. It is apparent that the

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composition at any point will be dependent upon local conditions and the history of that point. Therefore, the products which would be evolved from a non-uniformly heated plastic body would vary from point to point. In the case of the Century Series plastics, composition would also be influenced by local pressure. For G. E. 124 Resin, the compositions that are reported in this paper are not appropriate for high heat flux and high pressure. For such cases, one would probably be best off to assume that all available hydrogen is converted to H_2 and all available oxygen is converted to CO. Since the phenolics do not go through a foaming process during decomposition, the compositions which are reported for those materials are likely to be more representative of high heat flux, high pressure conditions.

In order to achieve better reproducibility for chemical analyses of the complex mixtures that are produced, one might set up elaborately developed gas chromatography systems. Analyses of the type that were performed would be required to back up the chromatography because of the complexity of the product picture. Still, it might be difficult or impossible to eliminate chemical reactions between products, and between products and the chromatography apparatus. An improvement over the arc image furnace and similar methods has recently been achieved by this author. Samples of plastics are flash pyrolyzed in the reaction chamber of the Bendix Time-of-Flight Mass Spectrometer. Mass spectra are photographed with 100 microsecond time resolution, so it will probably be possible to study free radicals and other transitory products. Such

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products are expected to be more representative of the primary high

temperature decomposition species than the stable products which have

been studied in the past and will probably furnish more information on

the mechanism of degradation. The mass spectroscopy technique has already

been used to study the more stable products which are present during the

first ten seconds after pyrolysis. These studies have shown that improved

reproducibility results from carrying out analysis soon after the products

form. It is also much easier to detect products which would disappear

later through chemical reaction. The results of time-of-flight mass

spectroscopy promise to be easier to interpret than those of arc image

furnace studies.

ACKNOWLEDGMENTS

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2. H. L. Friedman, G. E. TIS R61SD052, March 1961.

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TABLE 1

General Summary
(Including Yields of Non-Condensable Components and Ammonia)

Run		Exposure Time, sec.	Grams		Moles x 10^3						
			Total Weight Loss	Yield Third Fraction	Yield First Fraction	Yield Second Fraction	Yield H_2	Yield CO	Yield CH_4	Yield N_2	Yield NH_3
Glass Reinforced Phenolic											
33		5.0	.2464	.0421	-	1.705	-	-	-	-	0.988
37		10.0	.3576	.1100	9.029	1.938	5.581	2.546	0.876	0.028	0.897
38		10.0	.3674	.1209	9.523	2.334	5.913	2.685	0.895	0.028	0.966
51		10.0	.3538	.1144	8.826	2.122	5.436	2.322	1.041	0.026	1.055
52		10.0	.3468	.1099	8.765	2.030	5.337	2.358	1.034	0.035	1.020
Nylon Reinforced Phenolic											
34		10.0	.4602	.0887	7.385	6.548	4.505	2.068	0.805	0.007	0.785
39		10.0	.4541	.1192	7.718	7.072	4.724	2.192	0.787	0.012	0.859
40		10.0	.4521	.1234	8.066	7.051	5.009	2.249	0.791	0.016	0.858
49		10.0	.4469	.1096	7.694	7.035	4.762	2.093	0.824	0.014	0.763
50		10.0	.4503	.1237	7.729	7.597	4.646	2.188	0.881	0.016	0.823
G. E. 124 Resin											
25*		5.0	.1610	.0267	3.208	1.623	1.778	1.104	0.327	0.000	0
28		10.0	.4420	-	8.275	4.659	4.295	3.078	0.893	0.005	0
29		10.0	.4470	.1422	8.411	4.582	4.263	3.154	0.988	0.005	0
30		5.0	.1450	.0177	4.526	1.535	2.770	1.484	0.268	0.002	0
31		5.0	.1578	.0291	4.708	1.536	2.882	1.559	0.268	0.002	0
32**		5.1	-	-	4.935	1.578	3.045	1.624	0.266	0.001	0
35		10.0	.3370	.0976	7.604	3.622	4.357	2.616	0.624	0.007	0
36		10.0	.4105	.1377	7.917	4.642	4.267	2.873	0.768	0.009	0
41		10.0	.4393	.1196	7.929	4.445	4.527	2.816	0.569	0.005	0
42		10.0	.4486	.1012	7.976	4.402	4.458	2.896	0.614	0.005	0
53		10.0	.4497	.1222	8.499	4.951	4.505	3.179	0.791	0.026	0
54		10.0	.4475	.1188	8.459	4.812	4.559	3.104	0.779	0.016	0
56***		10.0	.3548	.1207	7.355	4.104	4.216	2.743	0.589	0.002	0

* Sample from different batch than other runs.
** Direct expansion of non-condensables into surge volume with diffusion pump not operating.
*** Sample from different batch than other runs.

TABLE 2

Detailed Product Analyses for Glass Reinforced Phenolic

Component	Fraction	Moles x 10^3		
		Run 38	Run 51	Run 52
Hydrogen	1	5.913	5.436	5.337
Methane	1	0.895	1.047*	1.034
Ammonia	2	0.984**	1.055	1.020
Water	3	-	4.931	1.152
Acetylene	2	1.293	0.842	-
Hydrogen Cyanide	2	0.231	0.235	-
Carbon Monoxide	1	2.685	2.322	2.358
Nitrogen	1	0.028	0.026	0.035
Ethylene	2	0.231	0.307	-
Ethane	2	0.014	0.042	-
Methanol	2	0.005	-	-
Propyne	2	0.035	-	-
Propylene	2	0.072	0.076**	-
Carbon Dioxide	2	0.040	0.141	-
Ethanol	2	0.005	-	-
Diacetylene	2	0.093	0.082	-
Vinyl Acetylene	2	0.044	0.024	-
Butadiene	2	0.012	-	-
Acetone	3	-	0.049	0.058
Isopropanol	3	0.026***	0.225	0.310
2-Pentene-4-yne	2	0.061	-	-
Cyclopentadiene	2	-	0.086	-
Benzene	3	0.135***	0.249**	0.549
Toluene	3	0.019***	0.046**	0.159
Phenyl Acetylene	3	-	0.011	-
Styrene	3	-	0.007	0.003
Xylenes	3	-	0.030**	0.076
Methyl Phenyl Acetylene	3	-	0.008	-
Methyl Styrene	3	-	0.006	0.002
C9 Aromatics	3	-	0.010	0.008
Dimethyl Styrene	3	-	0.001	-
Material Balance****, Per Cent				
		86.8	87.6	-

   *   Trace of methane in fraction 2.
  **   Parts of component in fractions 2 and 3.
 ***   In fraction 2.
****   Weight of three volatile fractions compared to total weight loss.

TABLE 3

Detailed Product Analyses for Nylon Reinforced Phenolic

Component	Fraction	Moles x 10^3		
		Run 39	Run 49	Run 50
Hydrogen	1	4.724	4.762	4.646
Methane	1	0.787	0.824	0.881
Ammonia	2	0.859	0.763	0.823
Water	3	-	0.026*	3.016
Acetylene	2	2.610	2.096	1.793
Hydrogen Cyanide	2	0.580	0.475	1.014
Carbon Monoxide	1	2.192	2.093	2.188
Nitrogen	1	0.012	0.014	0.016
Ethylene	2	2.355	2.487	3.480
Ethane	2	0.042	-	0.090
Propyne	2	0.141	-	-
Propylene	2	0.156	0.261	0.338**
Carbon Dioxide	2	0.446	0.435	0.408
Propane	2	0.057	-	-
Ethanol	2	0.057	-	-
Diacetylene	2	0.177	0.209	0.131
Vinyl Acetylene	2	0.134	-	0.106
Butadiene	2	0.106	-	-
Acrolein	2	-	0.839	-
Butylenes	2	-	-	0.069
Acetone	3	-	0.015*	0.137
Isopropanol	3	0.014*	0.011*	0.445
2-Pentene-4-yne	2	0.141	-	-
Cyclopentadiene	2	-	-	0.009
Pentenes	2	-	-	0.009
Benzene	2	0.113	0.168	0.218**
Toluene	2	0.014	0.013	0.097**
Phenyl Acetylene	3	-	-	0.080
Styrene	2	-	0.001	0.044**
Xylenes	2	-	0.001	0.062**
4-Ethenyl-1-Cyclohexane	2	0.002	-	-
Methyl Phenyl Acetylene	3	-	-	0.016
Methyl Styrene	3	-	-	0.008
C9 Aromatics	3	-	-	0.010
Dimethyl Styrene	3	-	-	0.001
C10 Aromatics	3	-	-	0.001
Material Balance***, Per Cent				
		98.5	99.8	102.7

* In fraction 2.
** Parts of component in fractions 2 and 3.
*** Weight of three volatile fractions compared to total weight loss.

TABLE 4

Detailed Product Analyses for G. E. 124 Resin

Component	Fraction	Moles x 10^3			
		Run 41	Run 42	Run 54	Run 56
Hydrogen	1	4.527	4.458	4.559	4.216
Methane	1	0.579	0.614	0.779	0.589
Water	3	-	-	3.865	5.435
Acetylene	2	1.551	1.228	-	0.616
Hydrogen Cyanide	2	0.018	0.013	-	-
Carbon Monoxide	1	2.816	2.896	3.104	2.743
Nitrogen	1	0.005	0.005	0.016	0.002
Ethylene	2	0.573	0.748	-	1.931
Ethane	2	0.044	0.040	-	0.064
Propyne	2	0.053	0.084	-	-
Propylene	3	0.244*	0.291*	0.094	0.220**
Carbon Dioxide	2	1.200	1.211	-	0.715
Propane	2	0.071	0.110	-	-
Ethanol	2	0.004	-	-	-
Diacetylene	2	0.102	0.062	-	0.061
Vinyl Acetylene	2	0.071	0.066	-	0.031
Butadiene	2	0.049	0.035	-	-
Acrolein	2	0.138	0.176	-	-
Butylenes	2	-	-	-	0.050
Acetone	3	-	-	0.040	0.170**
Propanal	2	0.102	0.128	-	-
Isopropanol	3	-	-	0.028	0.019
2-Pentene-4-yne	2	0.093	0.088	-	-
Cyclopentadiene	2	-	-	-	0.077
Pentenes	2	-	-	-	0.023
n-pentane	2	-	-	-	0.003
i-pentanes	2	-	-	-	0.049
n-butanol	3	-	-	0.105	0.033
Benzene	3	0.120*	0.101*	0.186	0.160**
Toluene	3	0.004*	0.003*	0.034	0.020**
Phenol	3	-	-	-	0.017
Phenyl Acetylene	3	-	-	0.018	0.010
Styrene	3	-	-	0.023	0.006
Xylenes	3	-	-	0.031	0.007
Methyl Phenol	3	-	-	-	0.007
4-Ethenyl-1-Cyclohexane	2	0.031	0.004	-	-
Methyl Phenyl Acetylene	3	-	-	0.036	0.013
Methyl Styrene	3	-	-	0.017	0.006
C_9 Aromatics	3	-	-	0.009	0.002
Dimethyl Phenol	3	-	-	-	0.004
Dimethyl Styrene	3	-	-	0.004	0.004
C_{10} Aromatics	3	-	-	0.003	-
Material Balance***, Per Cent					
		88.4	82.3	-	101.3

* In fraction 2.
** Parts of component in fractions 2 and 3.
*** Weight of three volatile fractions compared to total weight loss.

TABLE 5

Average Product Compositions and Molecular Weights

Component	Moles x 10^3			Mole Per Cent		
	Glass Phenolic	Nylon Phenolic	G. E. 124	Glass Phenolic	Nylon Phenolic	G. E. 124
Hydrogen	5.567	4.729	4.383	34.7	23.9	25.1
Methane	0.963	0.818	0.735	6.0	4.1	4.2
Ammonia	0.994	0.818	-	6.2	4.1	-
Water	3.042	3.025	4.650	18.9	15.3	26.6
Acetylene	1.068	2.166	1.132	6.7	10.9	6.5
Hydrogen Cyanide	0.233	0.690	0.010	1.5	3.5	0.1
Carbon Monoxide	2.478	2.158	2.940	15.4	10.9	16.8
Nitrogen	0.029	0.013	0.009	0.2	0.1	0.1
Ethylene	0.269	2.774	1.084	1.7	14.0	6.2
Ethane	0.028	0.044	0.049	0.2	0.2	0.3
Methanol	0.003	-	-	0.0	-	-
Propyne	0.018	0.047	0.046	0.1	0.2	0.3
Propylene	0.074	0.301	0.304	0.5	1.5	1.7
Carbon Dioxide	0.091	0.430	1.042	0.6	2.2	6.0
Propane	-	0.019	0.060	-	0.1	0.3
Ethanol	0.003	0.019	0.001	0.0	0.1	0.0
Diacetylene	0.088	0.172	0.075	0.5	0.9	0.4
Vinyl Acetylene	0.034	0.080	0.056	0.2	0.4	0.3
Butadiene	0.006	0.035	0.028	0.0	0.2	0.2
Acrolein	-	0.280	0.105	-	1.4	0.6
Butylenes	-	0.023	0.017	-	0.1	0.1
Acetone	0.054	0.142	0.078	0.3	0.7	0.4
Propanal	-	-	0.077	-	-	0.4
Isopropanol	0.281	0.453	0.024	1.7	1.3	0.1
2-Pentene-4-yne	0.032	0.047	0.060	0.2	0.2	0.3
Cyclopentadiene	0.043	0.003	0.026	0.3	0.0	0.1
Pentenes	-	0.003	0.008	-	0.0	0.0
n-Pentane	-	-	0.001	-	-	0.0
i-Pentanes	-	-	0.016	-	-	0.1
n-Butanol	-	-	0.069	-	-	0.4
Benzene	0.467	0.178	0.233	2.9	0.9	1.3
Toluene	0.112	0.093	0.029	0.7	0.5	0.2
Phenol	-	-	0.009	-	-	0.1
Phenyl Acetylene	0.006	0.080	0.014	0.0	0.4	0.1
Styrene	0.005	0.044	0.015	0.0	0.2	0.1
Xylenes	0.053	0.062	0.019	0.3	0.3	0.1
Methyl Phenol	-	-	0.004	-	-	0.0
4-Ethenyl-1-Cyclohexane	-	0.001	0.012	-	0.0	0.1

TABLE 5

(Continued)

Component	Moles x 10^3			Mole Per Cent		
	Glass Phenolic	Nylon Phenolic	G. E. 124	Glass Phenolic	Nylon Phenolic	G. E. 124
Methyl Phenyl Acetylene	0.004	0.016	0.025	0.0	0.1	0.1
Methyl Styrene	0.004	0.008	0.012	0.0	0.0	0.1
C9 Aromatics	0.009	0.010	0.006	0.1	0.1	0.0
Dimethyl Phenol	-	-	0.002	-	-	0.0
Dimethyl Styrene	0.001	0.001	0.004	0.0	0.0	0.0
C10 Aromatics	-	0.001	0.002	-	0.0	0.0
Total	16.059	19.783	17.471	99.9	99.8	99.8

Average Molecular Weight of Pyrolysis Gases, Gms/Mole		
Glass Phenolic	Nylon Phenolic	G. E. 124
19.08	23.16	22.01
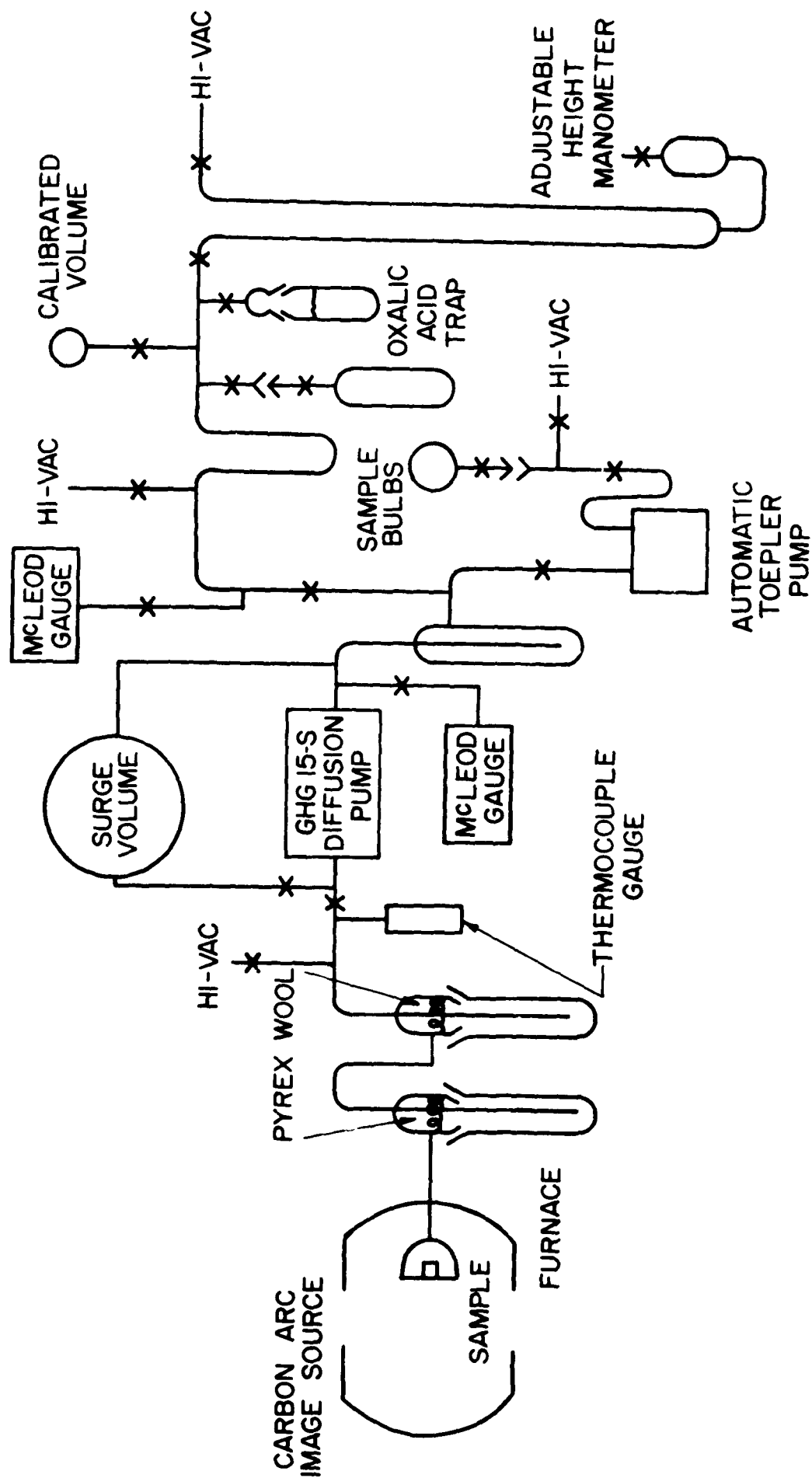
FIG. 1. ARC IMAGE FURNACE VACUUM SYSTEM

Outer Surface

FRONT SURFACE - 76X

Edge Surface

FRONT SURFACE - 583X

Interface

CHAR-PLASTIC INTERFACE - 154X

Center

INTERIOR CHAR - 76X

FIG. 2. MICROSTRUCTURE OF G.E. 124 RESIN CHAR AFTER 10 SECOND EXPOSURE - REFLECTED LIGHT

GENERAL ⬤ ELECTRIC

SPACE SCIENCES LABORATORY
MISSILE AND SPACE DIVISION

TECHNICAL INFORMATION SERIES

AUTHOR	SUBJECT CLASSIFICATION	NO.
Henry L. Friedman	Plastic Degradation	R62SD57
		DATE Dec. 1962

TITLE	
THE PYROLYSIS OF PLASTICS IN A HIGH VACUUM ARC IMAGE FURNACE. II.	**G. E. CLASS** I
	GOV. CLASS None

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SUMMARY

Samples of glass and nylon reinforced CTL 91-LD Phenolic and G. E. 124 Resin were pyrolyzed in an arc image furnace at high vacuum. Compositions of the various degradation gases are reported. Average molecular weights of these gases were calculated. A description of the mechanism of pyrolysis of G. E. 124 Resins is presented. A critique of the method is included.

By cutting out this rectangle and folding on the center line, the above information can be fitted into a standard card file.

AUTHOR _Henry Friedman_

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